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THESIS

IDENTIFICATION OF VOLATILE REACTOR FUEL DECOMPOSITION
PRODUCTS BY GAS CHROMATOGRAPHY AND SPECTRAL ANALYSIS

by

Leslie Winfred Cole

June 1968

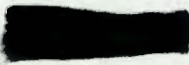
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IDENTIFICATION OF VOLATILE REACTOR FUEL DECOMPOSITION
PRODUCTS BY GAS CHROMATOGRAPHY AND SPECTRAL ANALYSIS

by

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Major, United States Army
B.S., East Tennessee State University, 1958


Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

from the

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June 1968

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ABSTRACT

The gases produced by irradiation of the polyethylene moderated fuel used in the AGN-201 reactor at the Naval Postgraduate School were analyzed for both radioactive and non-radioactive species. The hydrogen content of the gases is higher than that reported in the literature for the radio-induced degradation of polyethylene. Radioactive species identified are Kr^{85m} , Kr^{87} , Kr^{88} , Xe^{133m} , Xe^{133} , Xe^{135} , Xe^{138} , I^{131} , and Cs^{138} . Trace quantities of krypton and xenon were successfully separated without isotopic dilution using gas-solid chromatography.



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1. Introduction

The polyethylene moderated core of the AGN-201 Nuclear Reactor at the Naval Postgraduate School emits relatively large amounts of gases during and shortly after operation. These gases are subsequently released into the atmosphere. Measuring the constituents of these gases has presented numerous problems to past investigators. The various constituents are gaseous hydrocarbons, fission products, and possibly hydrocarbon-fission product compounds. The reactor fuel, 20% enriched UO_2 , is distributed throughout the polyethylene. Operation of the reactor decomposes the polyethylene by radiation and recoil of fission products.

The reactor core and rod voids are pressurized with nitrogen to approximately 1 psig when the reactor is operated. The gas is released periodically so that the total pressure in the core does not exceed 5 psig. The pressure rise is caused by the gaseous products from the degradation of the polyethylene. The radioactivity present in the gas is due to the gaseous fission products which have escaped from the core, but the small amount of these fission products do not add to the pressure.

Several investigators have reported that the bulk of the gas from the radioinduced degradation of polyethylene is hydrogen (1). Laskaris (2), using the same equipment available to this investigator, found that the hydrogen content of the gases was only approximately 50% of the total, with the remainder being light hydrocarbons to C_4 . Laskaris also attempted to determine the radioactive constituents by simultaneous gas chromatographic and radioactivity measurements of the gases. He successfully identified some of these constituents.

Laskaris and others at the Naval Postgraduate School (3,4,5) used gases taken directly from the core of the reactor. The reactor configuration requires the gases to diffuse from the relatively large, solid core through approximately 12 feet of copper tubing to a sampling manifold. The time necessary for this diffusion effectively prevents measurement of any of the parameters of the gases for several minutes. Additionally, the long copper tube offers a good surface for absorption and perhaps reaction of active species. The gases continue to diffuse from the large core for several hours after a reactor operation. Thus, at any time, there are gases present in the core produced by a prior reaction operation. The effect of the later irradiations on the gases is unknown. It was felt that the hydrocarbon content of the gases was likely to be sensitive to later irradiations.

Further analysis of the gases seemed in order, both to check the drastic deviation in regard to the proportion of hydrogen in the gases emitted from the reactor fuel and to more completely identify the radioactive constituents.

2. Experimental^{*}

a. Production of gases

In order to evaluate the gases resulting from a particular reactor operation, a small reaction vessel was constructed. This

^{*} Most of the work was done concurrently with Capt. L. A. Lindsay, US Army, whose thesis concerned the analysis of the same gases through a series of half-life studies on individual photopeaks of the radioactive species.

vessel could be placed in the access port in the reactor.*
Fuel identical to that in the core of the reactor was placed in the reaction vessel. The vessel was evacuated to 10^{-4} mm, and irradiated to obtain sufficient gases for analysis. The reactor fuel was evacuated prior to each irradiation to insure that only gases emitted during a single reactor operation were included in the study. The amount of gases and the total radioactivity resulting varied with the irradiation time and power, but no deviation of actual products was found, for the irradiation variations used.

b. Measurement of the non-radioactive species

The same gas chromatograph used by Laskaris was used in this study. It was necessary to establish the lower limits of sensitivity of the instrument since the experimental technique produced only very small samples. Ideally, the sample size for the instrument should be approximately 0.2 ml at atmospheric pressure. The pressure of the samples obtained in the experiment were in the range of 100 to 300 microns. The low pressure necessitated a sample volume of 2 ml. This was still much smaller than the ideal sample volume in number of molecules. This large sample volume with the resulting back diffusion during sample injection caused considerable baseline drift and poorly defined peaks.

* A complete listing of the equipment used in presented is Appendix I.

c. Measurement of the radioactive species

Several attempts were made to trap the radioactive species separated by the gas chromatograph, both with and without isotopic dilution, but all were unsuccessful.* Also, several attempts to measure the radioactive and chromatographic response simultaneously, as had been done by Laskaris, was unsuccessful. Apparently the small sample size with the resulting small amount of activity thwarted all efforts.

Kock and Grandy (6) described a method for separating xenon and krypton. Their method was modified and used in an attempt to separate these two gases from the other radioactive species. A pyrex glass column, approximately 20 by 60 mm was constructed and filled with 40/60 activated charcoal. The column interior and charcoal were evacuated to 10^{-4} mm. The column was connected to the reaction vessel as soon as possible after irradiation (approximately 15 minutes) and cooled to -196° C with liquid nitrogen. Valves on the reaction vessel were opened so the charcoal could absorb the gases for a period of 10 minutes. The reaction vessel was disconnected and helium forced through the charcoal at 400 ml/min. The column was removed from the liquid nitrogen and allowed to come to room temperature as the helium flow started. The effluent gases flowed through a 1/4 in tube and around a 2 by 2 inch scintillation crystal shielded by 2 inches of lead. The crystal acted as a chromatographic detector and its output was monitored by a count rate meter. The effluent

* A method for trapping the gases was later developed but was not attempted with the gases separated with the gas chromatograph.

gases, after passing the scintillation crystal, were forced into a 3/16 by 6 inch activated charcoal trap cooled to -196°C . As soon as the first radioactive species had passed, as indicated on a chromatogram, the charcoal trap was changed. The charcoal containing the original sample was then heated rapidly to approximately 300°C . Another peak appeared almost immediately. The two peaks were subsequently identified as krypton and xenon, respectively. Gamma ray spectrometry measurements were made on the radioactive species remaining in the large column.

3. Results

a. Non-radioactive species

Figure 1 is a typical chromatogram measured by Laskaris. Figure 2 shows a comparative chromatogram measured with the much smaller sample described above. The general agreement is excellent. The calculated proportions by volume per cent of the various hydrocarbons and hydrogen measured by chromatographic methods are shown in Table I. The values found in this study compare favorably with those found by Laskaris. The difficulty in making accurate quantitative measurements on a chromatogram such as Figure 2 tend to make these results less reliable, however there is a significant amount of hydrocarbons in the gaseous mixture. This is of importance in view of the reports in the literature of the much higher content of hydrogen in the degradation products of polyethylene.

TABLE I
VOLUME PER CENT COMPOSITION OF VOLATILE PRODUCTS

	Laskaris*	Cole*
Hydrogen	52.5	60.0
Ethane	13.0	17
Ethylene		
Methane	15.0	19.0
Propane	2.0	1.5
Cyclopropane	1.0	0.5
Propylene	3.5	trace
N-Butane	2.5	1.0
Isobutane	0.5	0.7
2-Butene	0.5	-
1,3-Butadiene	0.5	trace
Acetylene	3.0	trace
Krypton	0.5	-
Xenon	0.5	-

*Average of several different runs; does not total 100%

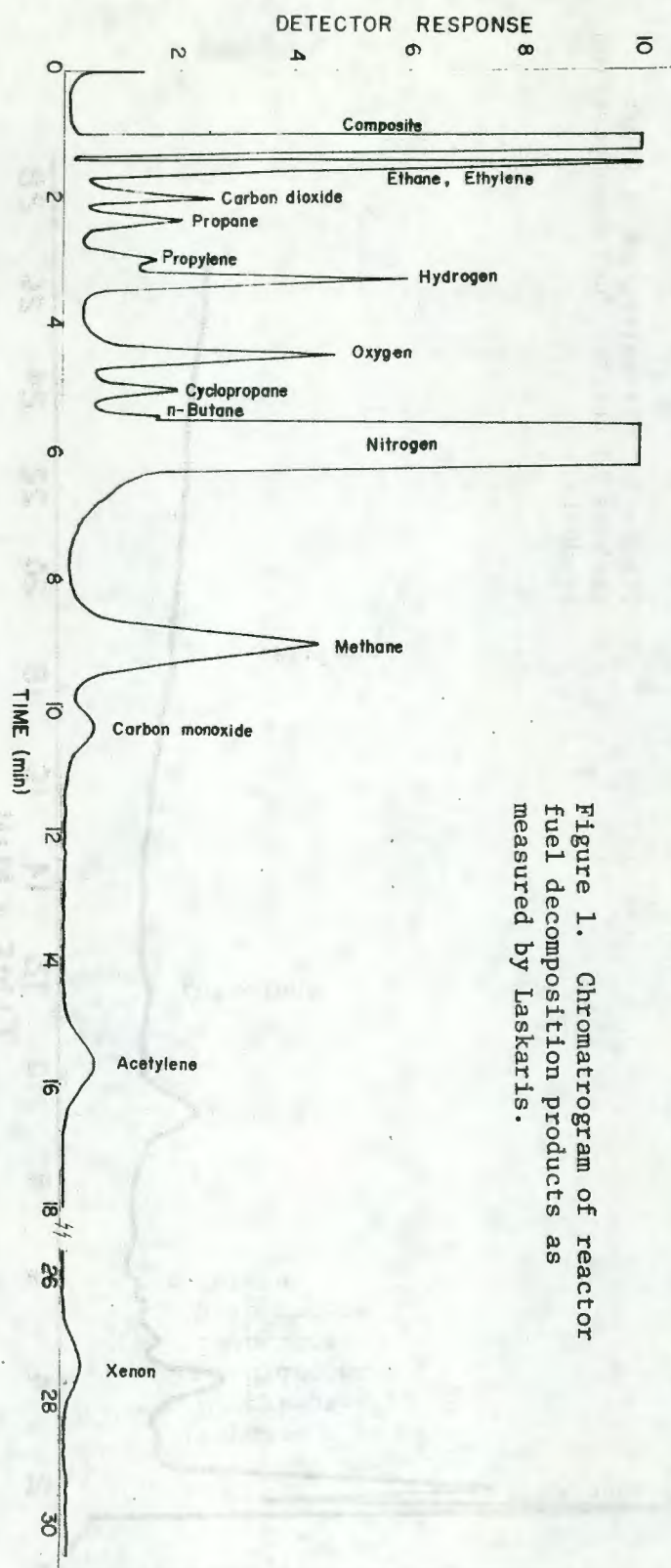


Figure 1. Chromatogram of reactor fuel decomposition products as measured by Laskaris.

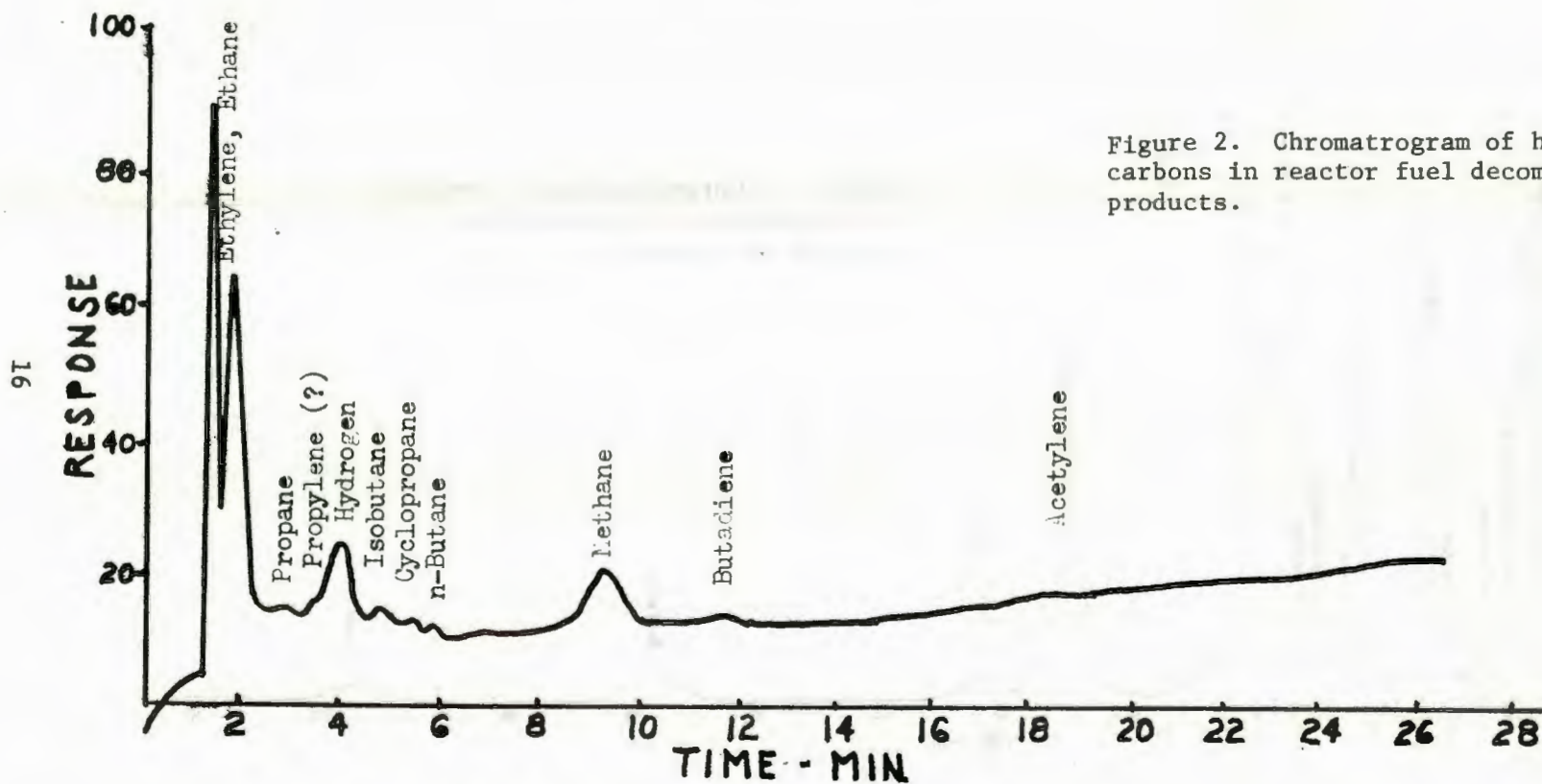


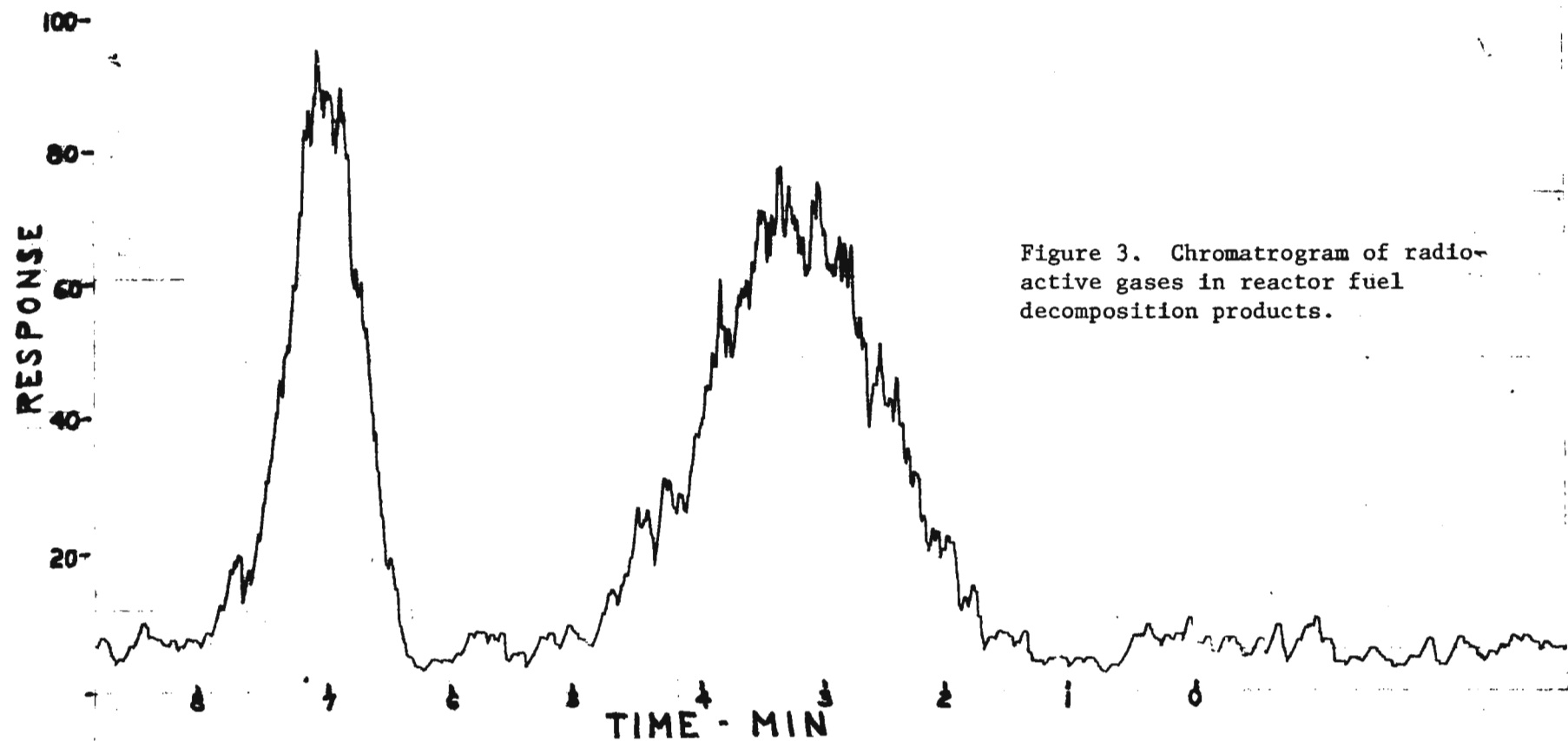
Figure 2. Chromatogram of hydrocarbons in reactor fuel decomposition products.

b. Radioactive species

A chromatogram made with the scintillation crystal detector is shown in Figure 3. The first peak is quite broad but there is little doubt that it is krypton as shown by the gamma ray spectrum of the trapped gas (Figure 4). This spectrum was measured only 2 minutes after the trap was removed from the chromatograph and only 36 minutes after the irradiation had been completed. The second peak is much sharper as the result of the much higher temperature while it was being eluted. A gamma ray spectrum of this gas is shown in Figure 5. This measurement was made 51 minutes after the irradiation and 15 minutes after separation. Xenon and some of its decay products are clearly identifiable.

Gamma ray spectra of the separated gases taken at later times revealed no radioactive species other than the krypton or xenon and their decay products. Also no other radioactive species could be eluted from the original sample in 30 minutes at 300°C.

The first peak could possibly be made sharper and could have been eluted earlier at a somewhat higher temperature. This was not attempted as the separation seemed adequate. Dal Nogare and Juvet discuss the effect of increased temperature on elution time and peak sharpness (6). A point of particular note about this separation is that the gases present were only those present as the result of the irradiation of the fuel. Isotopic dilution was not necessary for the separation.



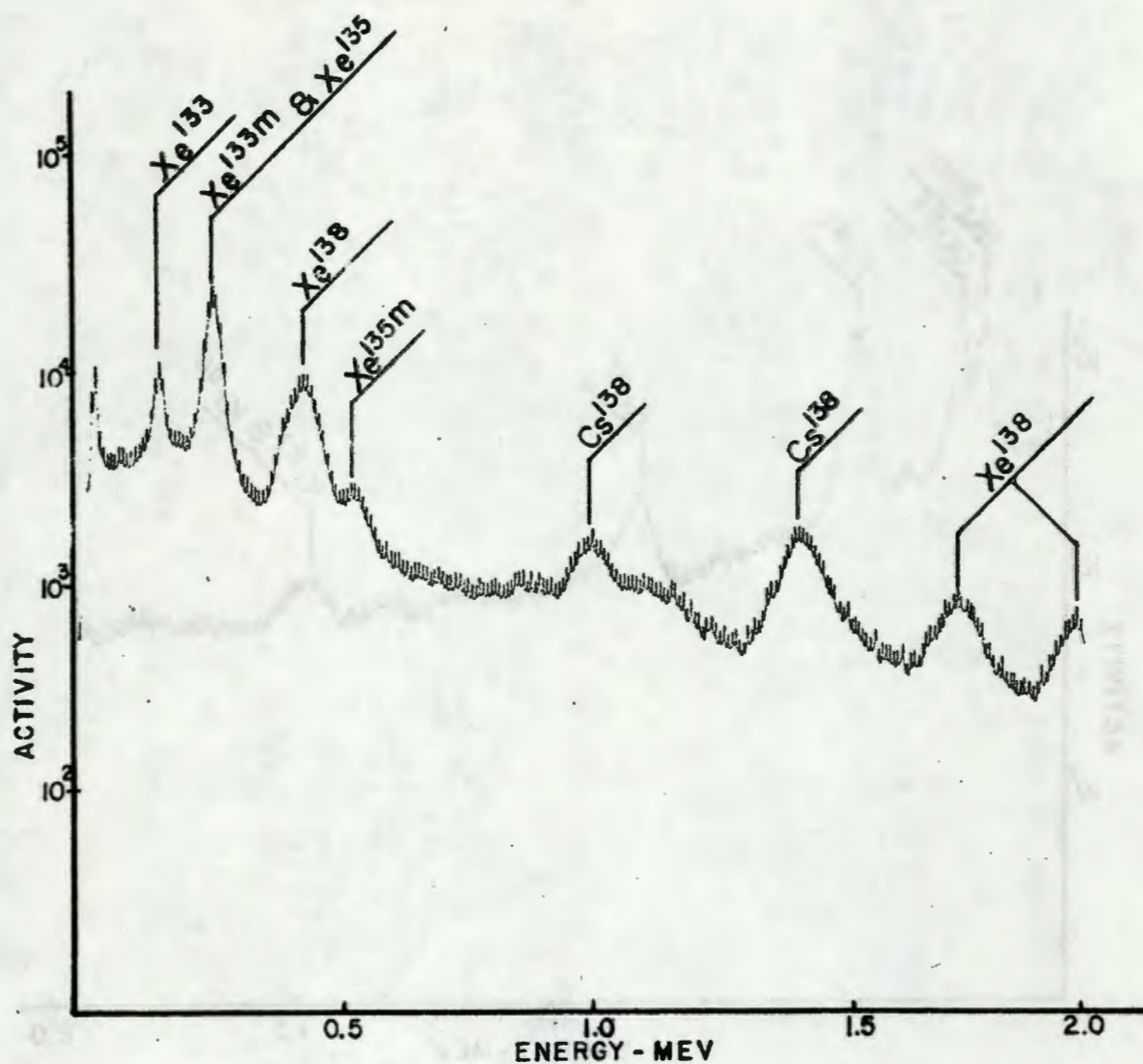


Figure 4. Gamma ray spectrum of krypton trapped after chromatographic separation. Measurement made approximately 36 minutes after irradiation and 2 minutes after separation.

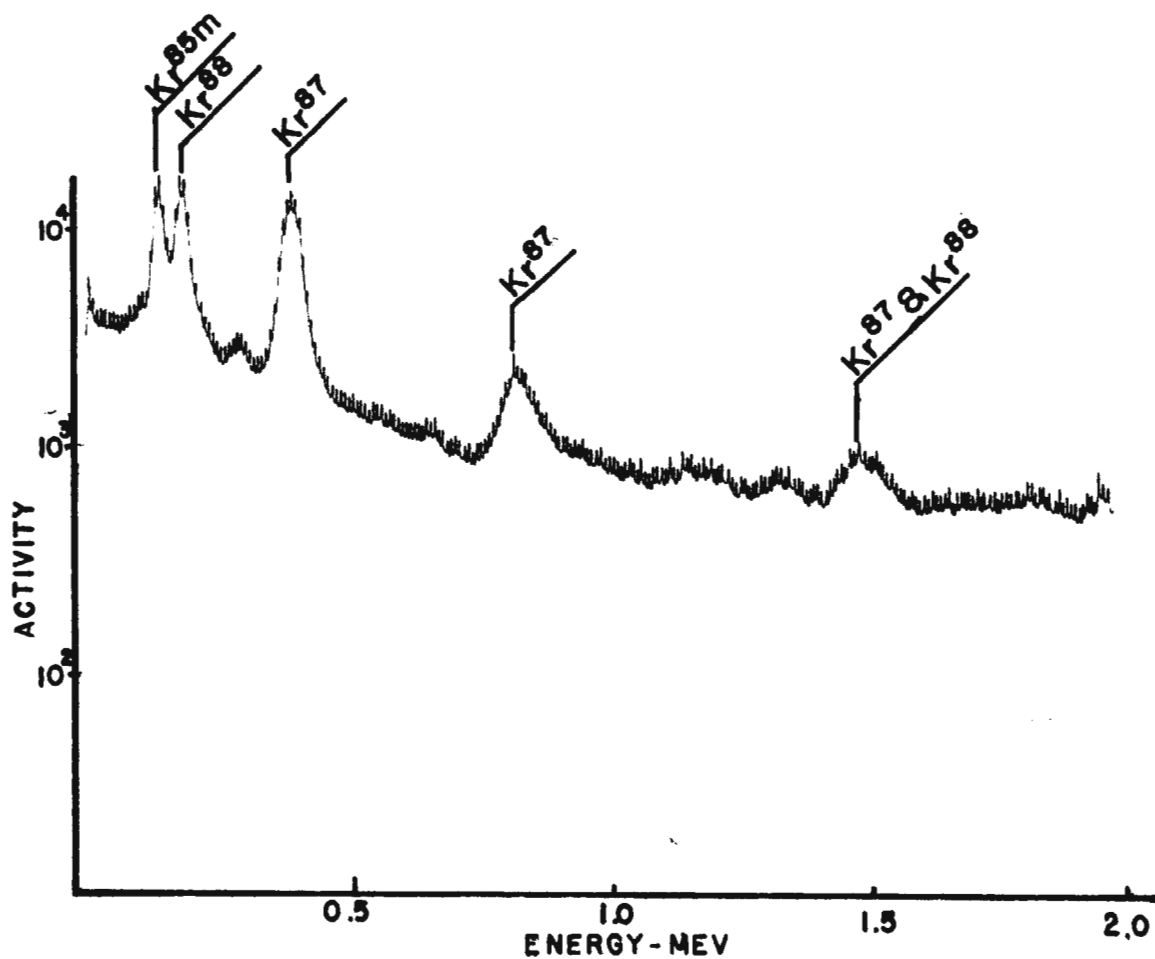


Figure 5. Gamma ray spectrum of xenon trapped after chromatographic separation. Measurement made approximately 51 minutes after irradiation and 15 minutes after separation.

The eluted gases contained most of the activity of the original sample. Some activity still remained on the charcoal column, however. Gamma spectra of the remaining active species are shown in Figure 6. Initially only the decay products of xenon and krypton were identifiable. Later, two iodine isotopes were evident and still later, Figure 7, another iodine isotope is identifiable.

A list of all the radioactive species identified is presented in Table II. Half lives used in the identification were determined using the computer program Frantic II, developed at M.I.T.(7).

4. Discussion

a. Proposed mechanism of polyethylene degradation

The agreement with Laskaris on the amount of hydrogen present in the degradation products is good and quite different than that generally reported (1). This indicated that the mechanism proposed in the literature is incorrect or the conditions in this study are sufficiently different to cause a different reaction. The latter would appear to be the case as the conditions in this experiment are different than any found in the literature.

While no studies were undertaken to specifically identify the mechanism of the polyethylene degradation in the AG-201 reactor fuel, the following seems logical in view of the products formed. The AGN-201 fuel as mentioned earlier, contains the UO_2 evenly distributed throughout the polyethylene. When undergoing fission, the massive fission products subject the polyethylene to more severe ionizing effects than other irradiation techniques. Scissions

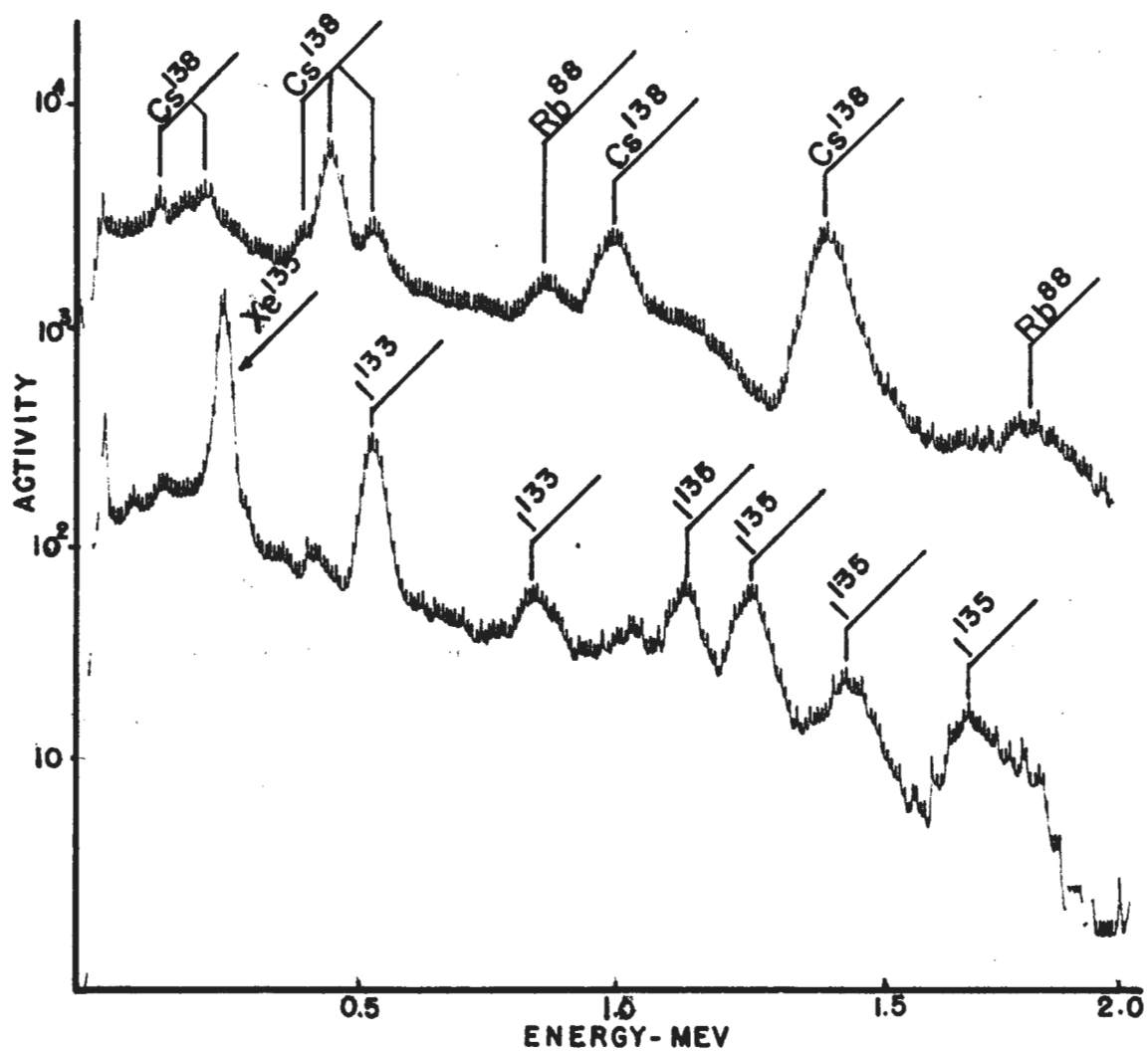


Figure 6. Gamma ray spectra of species not eluted from charcoal during gas chromatographic separation. Spectrum 1 measured at 44 minutes after irradiation; spectrum 2 at 425 minutes after irradiation.

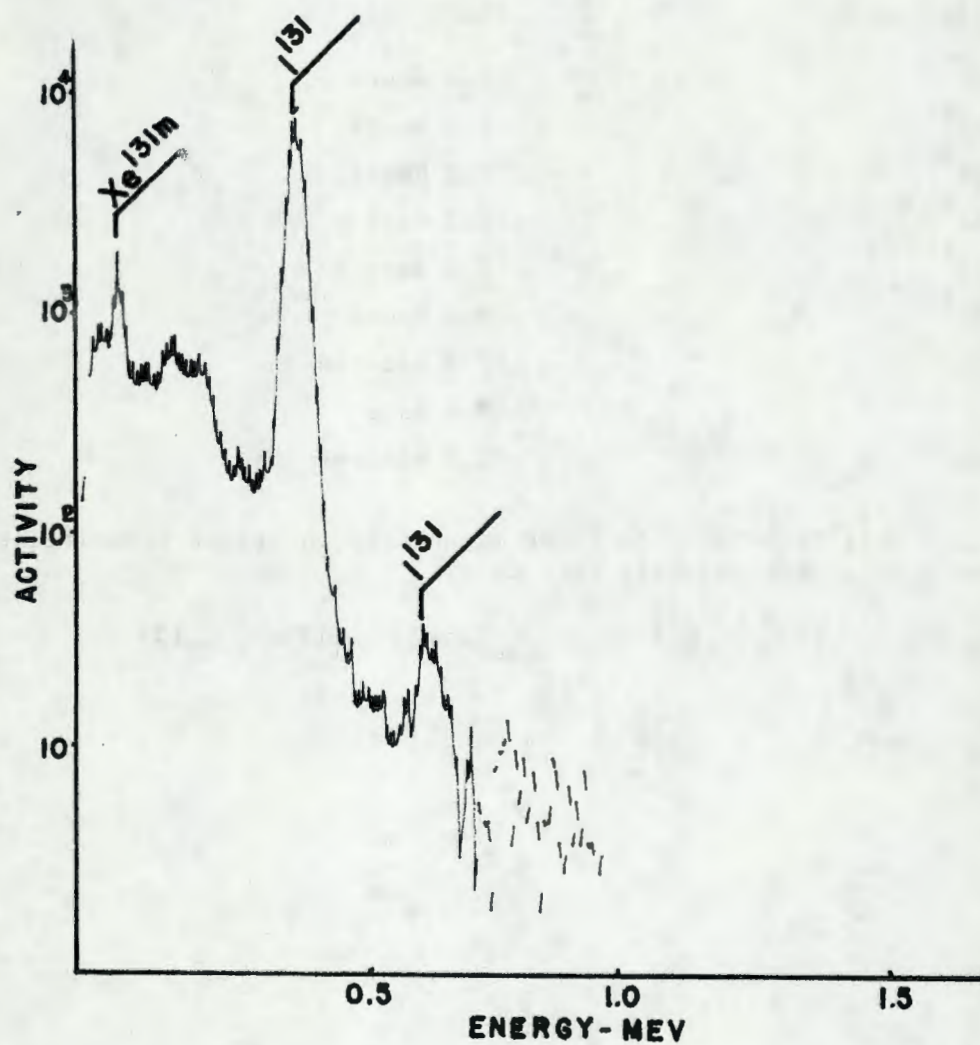


Figure 7. Gamma ray spectrum at species not eluted from charcoal during gas chromatographic separation. Measurement at 6 1/4 days after irradiation.

TABLE II
RADIOACTIVE SPECIES IDENTIFIED IN THE
REACTOR FUEL DECOMPOSITION PRODUCTS

A. Well identified isotopes

Isotope	Half-life
Kr ^{85m}	4.4 hours
Kr ⁸⁷	1.3 hours
Kr ⁸⁸	2.8 hours
Xe ^{133m}	2.3 days
Xe ¹³³	5.3 days
Xe ¹³⁵	9.2 hours
Xe ¹³⁸	17.0 minutes
I ¹³¹	8.0 days
Cs ¹³⁸	32.2 minutes

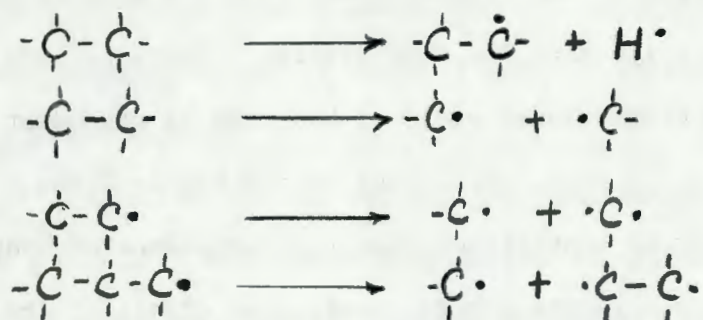
B. Less well identified isotopes (generally photopeak identification only-no supporting half life data)

Rb⁸⁸ Rb⁸⁹ Xe^{131m} Xe^{135m} I¹³³ I¹³⁵

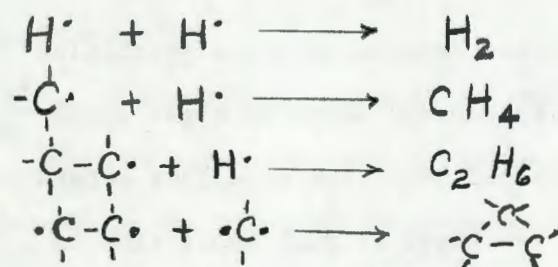
along chains, breakage at side-chain junctions, and further ionization of the newly formed fragments should all occur.

Likely steps leading to the various hydrocarbons are:

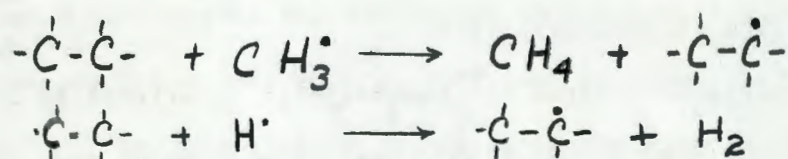
1. Formation of radicals



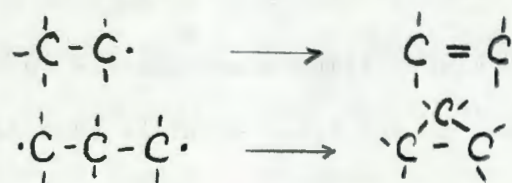
2. Radical combination



3. Abstraction of H^{\cdot}



4. Radical Disproportionation



The proposed steps in the reaction are very similar to those by several investigators, e.g., Miller et.al. (8), the principal difference being the larger amount of fragmentation. As stated earlier the more severe ionizing effect of the massive fission fragments can be expected to produce more fragments than perhaps gamma radiation used for most studies. There is some evidence that the proportional yield of hydrogen is dependent on the total radiation dose, decreasing at the higher doses. This would support the supposition that the difference of hydrocarbon content is due to the greater ionization effect of the fission fragments.

b. Separation of xenon and krypton in trace quantities

The separation of krypton and xenon by a gas-solid chromatographic technique is not new. The excellent separation of trace quantities of the two gases in such short time is significant. The gamma spectra of the trapped gases are very accurate aids in identification.

It should be pointed out however that an attempt to detect xenon as it eluted at about 95°C was not successful even though it was trapped in the same manner as described above. Apparently at that temperature the elution of the xenon is too slow to be practically detected. The higher temperature appears to be necessary to elute the xenon in the trace quantity used in this study.

c. Identification of halogens that may be present

Iodine and bromine were both suspected as being present in the gaseous products. It had been hoped that separation of

the xenon and krypton from the remaining volatile products would allow their identification. As expected, the more active decay products of short half life xenon and krypton isotopes dominated the gamma ray spectra initially. Iodine was identified after most of the xenon and krypton daughters had decayed sufficiently. No bromine could be identified even then. Bromine 83 is the only bromine isotope that could likely have been present at the time the later gamma spectra were measured, as the other shorter life isotopes would have decayed completely by that time. A more rapid sampling and separating technique may enable one to more accurately identify species other than krypton and xenon.

Since iodine is detectable in the volatile products, the question immediately arises as to its form. While it is entirely possible that it could be molecular iodine, this seems quite unlikely in view of the large amount of atomic hydrogen and organic radicals likely present during irradiation. It logically appears that any iodine present would be in the form of hydrogen iodide or low hydrocarbon compounds such as methyl iodide.

5. Conclusions

a. The irradiation of polyethylene by an internal source, i.e., the UO_2 in the AGN-201 fuel, results in a lower ratio of hydrogen to hydrocarbon than irradiation using an external radiation source. This is apparently caused by the large number of highly ionizing fission particles which increase the actual ionizing dose to which the polyethylene is subjected during irradiation.

b. The amount of xenon and krypton produced in the relatively small sample of AGN-201 fuel by short irradiation can be separated by solid-gas chromatography and detected by scintillation counting techniques without isotopic dilution.

c. Iodine is present in the volatile products from the AGN-201 fuel.

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APPENDIX I

List of Equipment Used

Gas Chromatograph: Fisher-Hamilton Model 29 Gas Partitioner with a 6 ft. x 1/4 in. 30% Hexamethyl-phosphoramide (HMPA) on 60/80 mesh columnpack in position 1 and a 12 ft. x 1/4 in. composite two part column consisting of 5 ft. of uncoated 60/80 mesh columnpack followed by 7 ft. of 42/60 mesh activated molecular sieve 13X in position 2.

Recorder for Gas Chromatograph: Varian Model 14, 1 millivolt recorder.

Scintillation Crystal and Associated Equipment:

2 in. x 2 in. NaI(Tl) crystal
DuMont Type 6292 Photomultiplier Tube
Hewlett-Packard Preamplifier Model
Technical Associates Rate Meter Model FM 1

Vacuum System: A glass vacuum system with a CENCO HYVAV 2 pump and an oil diffusion pump. Pressure measurement: Thermo-couple gauge calibrated to 1 micron. (Pressures actually used were lower than this and were estimated to be 10^{-4} mm when the meter was "pegged").

Reaction Vessel: A cylindrical aluminum container approximately 2 x 5 in. fitted with a vacuum stainless steel valve. (It proved necessary to attach a high vacuum stopcock to the valve in order to maintain the desired vacuum when the vessel was disconnected from the vacuum system for irradiation.)

Fuel: 8 grams of UO_2 in approximately 200 grams of polyethylene.

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Hydrogen
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